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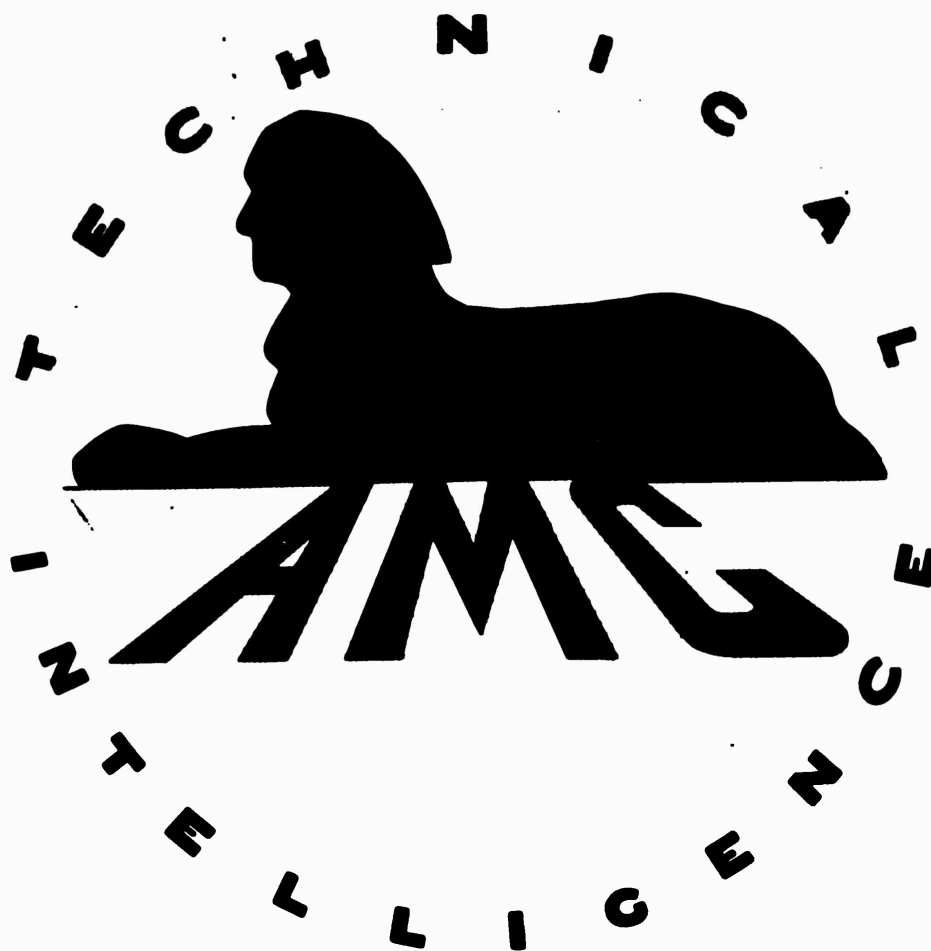
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CWS-NDRC TECHNICAL PROGRAM

DIVISION B

NATIONAL DEFENSE RESEARCH COMMITTEE

OF THE

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

Report on "Volatility of Levinstein Mustard"
to
September 31, 1942
by
Dr. H. E. Bent, Professor of Chemistry at
University of Missouri

OSRD No. *1062*

Serial No. 439

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Serial No. 439

CWS-NDRC TECHNICAL PROGRAM

DIVISION B

NATIONAL DEFENSE RESEARCH COMMITTEE

OF THE

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

Section B-3-B

Report on "The Volatility of Levinstein Mustard" (CWS-6).

Endorsement (1) from Warren C. Johnson, Member Section B-3-B, to
C. S. Marvel, Chairman, Section B-3. Forwarding report and noting:

> "The vapor pressure of Levinstein Mustard has been
> determined at $40°$ C. and over an appreciable range
> of composition of the ingredients. It has been
> found that the mustard sample contains approximately
> 1% of a relatively high volatile material which
> possesses a volatility about three times that of
> pure mustard. The following 9% of the sample shows
> very little change in volatility and its value is
> about 0.9 of that of pure mustard. The data obtained
> in this study are compared with those previously ob-
> tained for pure mustard. The sample of Levinstein
> Mustard studied was from the ordinary plant-run
> material manufactured by Edgewood Arsenal. The data
> may be of interest in a consideration of certain
> field problems dealing with the use of mustard gas."

(2) From C. S. Marvel, Chairman, Section B-3 to
Roger Adams, Chairman, Division B. Forwarding report and
concurring:

(3) Twenty-eight copies forwarded to Dr. Irvin
Stewart, Secretary of the National Defense Research Committee,
as Progress Report under Contract- (B-236, OEMsr-312) with the
University of Missouri.

Roger Adams, Chairman
by Harris M. Chadwell
Technical Aide

"THE VOLATILITY OF LEVINSTEIN MUSTARD"

by

H. E. BENT

ABSTRACT

The first one percent of a sample of Levinstein Mustard
(obtained from Edgewood Arsenal) removed by vaporization has
been found to give a volatility approximately three times that
of pure mustard. Upon the successive removal of small amounts
of the material by volatilization, the next nine percent shows
very little change in volatility, and gives a value approxi-
mately nine-tenths that of pure mustard. This report gives a
comparison of volatility data of Levinstein Mustard with
those of pure mustard as submitted in a previous report. The
data, of necessity, represent values for finite amounts of the
components removed in the vaporization. If it is assumed that
Raoult's law is obeyed by the most volatile component, then
upon extrapolation it is estimated that the most volatile con-
stituent has a volatility approximately one hundred times as
great in the pure state as when dissolved in Levinstein Mus-
tard, or approximately two hundred times as great as pure
mustard. This suggests that the most volatile constituent is
a substance of a rather small molecular weight.

During the course of the experiments it was observed that
the amount of solid material precipitating from the liquid in-
creased. On the basis of the fact that the volatility was
found to become constant and gave a value of about nine-tenths

that of pure mustard, it may be concluded that the amount of
non-volatile impurity in solution in the Levinstein Mustard is
at a concentration of approximately 0.1 mole fraction.

Aside from the fact that there is a difference in the
volatility of Levinstein and pure mustard samples, the informa-
tion is of interest in other respects. In the study of the
toxicity of different types of mustard gas, this difference in
volatility is an important factor, depending upon the type of
procedure used to carry out the toxicity measurements. In
addition, in the dispersal of mustard gas in the atmosphere by
high altitude sprays or by other means, it is of importance to
know the volatility of the material used. It is of particular
importance to be aware of the fact that the amount of solid
material dissolved in the Levinstein Mustard reduces the
volatility approximately ten percent.

(The experimental work of this report was carried
out by Mr. Irby M. Bunding of the University of Missouri.)

DISCUSSION

Problem.   The volatility of Levinstein Mustard is to be studied in order to determine how this varies with the amount of material removed by vaporization. A single tube supplied by Edgewood Arsenal was available for the experiment. This was divided into two portions in order to obtain better check on the shape of the curve. The sample was very dark in color and the tube contained a solid mass which was practically insoluble in acetone. The supernatent liquid was used but at the conclusion of the experiments more solid was present.

Experimental.   Details of the experimental procedure have been given in two previous formal reports* In this particular study the weight of sample introduced into the saturator was recorded in order that the data could be expressed in terms of the fraction of the sample volatilized. All measurements were carried out at 40° C, this temperature being convenient experimentally. We will assume that the ratio of the volatility of Levinstein mustard to pure mustard at all working temperatures will not vary from the value at 40° by a significant amount. A small correction would be required due to a difference in the heat of vaporization of the impurity and the mustard in going from one temperature to another, but the crudeness of the sample would hardly justify such a correction or the equivalent procedur of measuring the sample at two temperatures. Levinstein mustard will froth in the saturator at moderate rates of flow of gas. At lower velocities of gas flow this was not serious.

* Formal Reports, Serial Nos. 427 and 436 by H. E, Bent.

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<u>Results.</u>   The tables give the experimentally determined volatility and also the volatility expressed as a percentage of that for pure mustard. The graph gives values for the experimental data, plotted in a manner to be indicated below, and also a curve which indicates the volatility as a function of the composition.

In **choosing** a value for the abscissa for the plot, consideration must be given to the fact that at the beginning of the series the volatility is changing rapidly. Each run is, therefore, an average of a high volatility at the start and a low volatility at the conclusion of the run. This experimentall observed volatility, which is an average, is then plotted against the amount of mustard removed, expressed as percent of the sample, when half of the sample has been collected. Similarly the second volatility is plotted as ordinate against a value for the abscissa which represents the total amount of mustard removed when half of the second run had been collected. If the volatility were a linear function of the amount of material removed, a curve connecting points plotted as above would give the true volatility as a function of composition. As will be noted from the curve, however, there is a very rapid decrease in volatility with a resulting sharp curvature which indicates that the true volatility curve should fall somewhat to the left of the experimental points. This has been suggested by the full line drawn on the graph.

Since the very volatile fraction constitutes not more than one percent of the sample one may conclude that the remaining 99% of the sample will obey Raoult's law and will have a volatility of 99% of what it would have in the absence of the volatile component. We may, therefore, split up the total volatility, which is 300% of that of pure mustard into two parts, the first being that due to the less volatile material which has essentially the same volatility as pure mustard and the remaining 1% of the liquid which must therefore account for a volatility of approximately twice that of mustard in order that the total will be three times that of pure mustard. If we now assume that Raoult's law is obeyed by this volatile component, which is only a rough approximation for a substance in small concentration, then we can estimate that if this material were isolated it would have a volatility approximately one hundred times as great as in Levinstein mustard or a volatility two hundred times as great as pure mustard. At 40°C this would be something like 500 mg per liter. This suggests a substance of rather small molecular weight.

The non-volatile impurity, much of which crystallized in the container before and during the run has not been analyzed. Judging from the fact that the final volatility is nine tenths of that of pure mustard we may conclude that at least a mole fraction of one tenth is to be assigned to the non volatile impurity. Any volatility assigned to impurities present near the conclusion of the experiment would lead to the assignment of a

value somewhat greater than one tenth to the concentration of the impurity.

EXPERIMENTAL VALUES FOR THE VOLATILITY OF
LEVINSTEIN MUSTARD EXPRESSED AS MG PER LITER AT 40°C

	Run I			Run II	
Wt. of sample	Amt. Collected	Volatility	Wt. of sample	Amount Collected	Volatility
7.27	0.14763	5.952	12.9	0.17487	3.193
	.02196	1.034*		.05912	2.752
	.07112	3.362*		.05481	2.556
	.05370	2.527		.05280	2.489
	.05343	2.519		.05385	2.496
	.05645	2.658			
	.05158	2.409			
	.05432	2.532			
	.05294	2.507			
	.05296	2.463			
	.05158	2.428			

*During the second determination of the first run the heater wire on the exit tube of the saturator became detached with resulting condensation between the saturator and the collecting trap. This causes the second value to be low and the third high but does not affect the remainder of the runs. Some of the inconstancy in the values of later runs is doubtless due to the supersaturation of the solution and later crystallization of impurities.

COMPARISON OF THE VOLATILITY OF LEVINSTEIN WITH

PURE MUSTARD (2.74) AND A TABULATION OF DATA

USED FOR THE GRAPH.

Run I		Run II	
% of the sample remaining when half of a given determination had been completed	Volatility expressed as % of that of pure mustard	% of the sample remaining when half of a given determination had been completed	Volatility expressed as % of that of pure mustard
98.98	254	99.32	300
		98.42	100
		97.97	93
96.32	92	97.56	91
95.58	92	97.14	92
94.83	97		
94.08	89		
93.36	92		
92.62	91		
91.89	90		
91.17	89		

Conclusions

Data have been obtained over the range of composition for which the volatility is changing most rapidly. There is no indication the volatilization of a large fraction of the sample would give anything of interest. One might expect, however, that the last of the sample to vaporize would give a much lower volatility due to the accumulation of impurities. This range of composition could be studied if much larger samples were available.

Submitted by: H. E. Bent
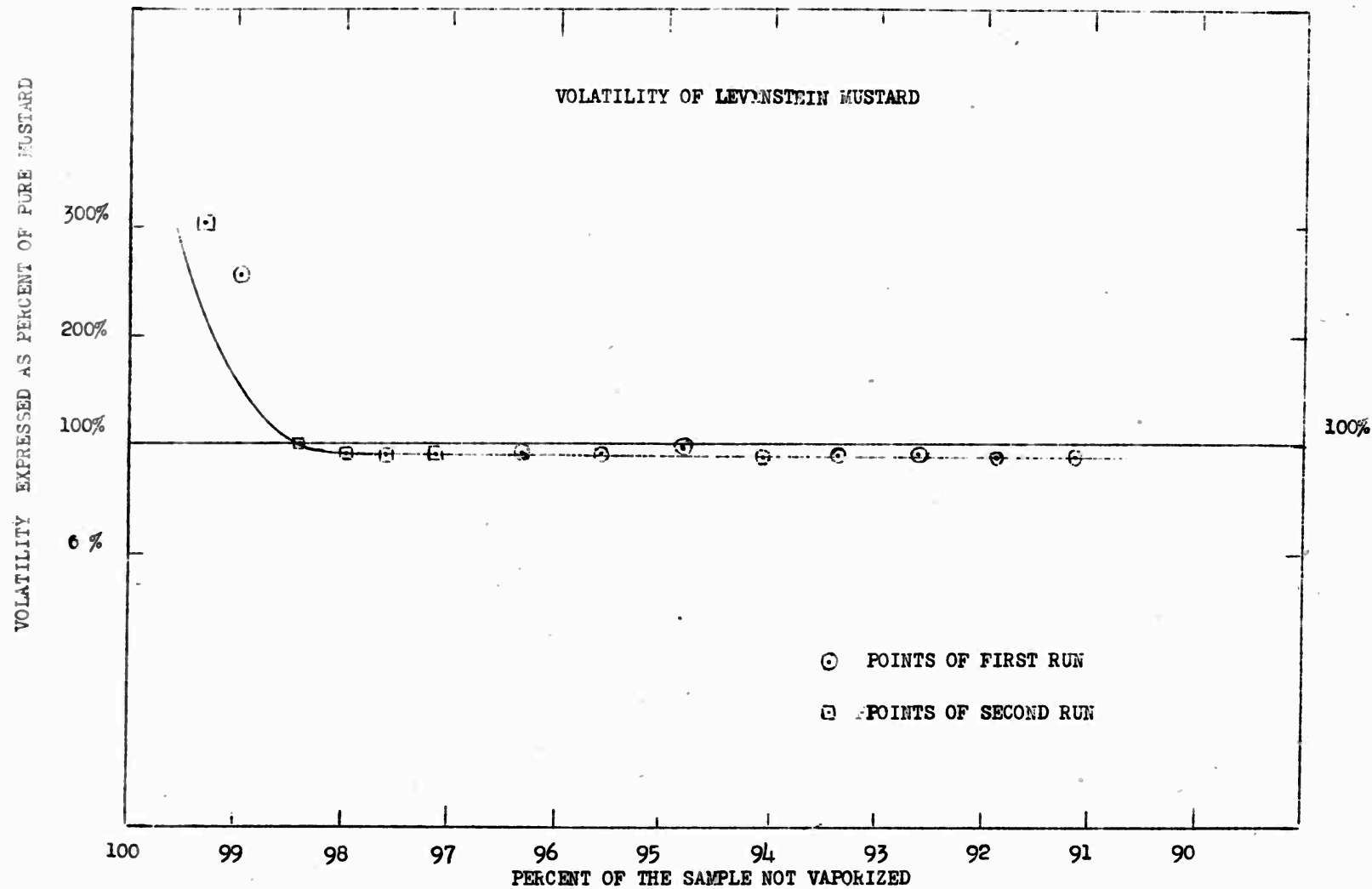
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ABSTRACT:

The vapor pressure of Levinstein mustard was determined at 40°C and over an appreciable range of composition of the ingredients, to determine how the volatility varies with the amount of material removed by vaporization. The mustard sample was found to contain approximately 1% of material which possesses a volatility about three times that of pure mustard. The following 9% of the sample showed very little change in volatility, and its value is about 0.9 that of pure mustard. The amount of non-volatile impurity in solution in the Levinstein mustard is at a concentration of approximately 0.1 mole fraction. The data are compared with those previously obtained for pure mustard, and may be of interest in a consideration of certain field problems dealing with the use of mustard gas.

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